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Novel rhenium-based catalysts for dehydrocondensation of methane with CO/CO_2 towards ethylene and benzene

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A new family of rhenium-based catalysts bearing HZSM-5 zeolite exhibits remarkable performances for the catalytic dehydrocondensation of methane with CO/CO_2 towards ethylene, benzene, and naphthalene in high selectivity of above 90% at 1–3 atm and 973–1023 K. In contrast to Mo/HZSM-5 catalysts, the EXAFS and TG/DTA/Mass studies reveal that the metallic Re on HZSM-5 zeolite is a catalytically active and stable phase for the reaction.

Keywords: methane, dehydrocondensation, benzene, ethylene, Re catalyst, HZSM-5

1. Introduction

The direct conversion of methane to petrochemical feed stocks such as aromatics such as benzene and naphthalene has recently attracted considerable attention [1–18]. Since the initial discovery [1,2] in 1993–1995, there has been a general agreement [10,14–17] that molybdenum-supported HZSM-5 zeolite exhibits uniquely non-oxidative conversion of methane to aromatics such as benzene and naphthalene with benzene selectivities of 43–60% based on the consumed methane at higher temperatures of 973–1023 K, although methane conversion was drastically suppressed and the catalysts were deactivated in a few hours due to serious coke formation. Ichikawa et al. [13,14] recently reported that adding of several percents of CO or CO_2 in the methane flow results in a remarkable stability of catalytic methane conversion to benzene in the prolonged time-on-stream of over 2000 min at 973 K on Mo/HZSM-5 and Co- and Fe-modified Mo/HZSM-5 catalysts owing to the substantial suppression of coke. Nevertheless, so far other transition metals such as Fe, V, Co and W besides molybdenum show modest methane conversion and similar formation selectivity to aromatics such as benzene and naphthalene [7,10,16,18].

Here we describe a new family of active catalysts based on rhenium-bearing HZSM-5 zeolite in the catalytic dehydrocondensation of methane (or preferably with CO/CO_2) to ethylene, benzene, and naphthalene with up to 10% conversion and selectivity of above 90% at 1–3 atm and 973–1023 K.

2. Experimental

A 5% loading rhenium on HZSM-5 (5%Re/HZSM-5) was prepared by the incipient wetness method as follows. In a container, 5.0 g of the ammonium form of ZSM-5, having a SiO_2/Al_2O_3 ratio of about 40 and a surface area of about 925 m^2/g (obtained from Toso Co.) were contacted with 5 ml of an aqueous solution of NH_4ReO_4. The impregnated support was subsequently dried at 393 K and then calcined at 773 K for 6 h. A 5%Re–0.5%Co/HZSM-5 catalyst was prepared by the subsequent impregnation of 5%Re/HZSM-5 with $Co(NO_3)_2$ aqueous solution, followed by drying and calcination. Re/HZSM-5 was pre-reduced with H_2 at 573 K for 1 h prior to the methane reaction. The conversion of methane with or without CO/CO_2 was carried out at 1–5 atm at 873–1023 K by a fixed-bed continuous-flow system with a quartz reactor of 8 mm i.d., in which 0.3 g of catalyst was charged. The effluent gases were analyzed by FID and TCD gas chromatographs. Hydrocarbon products including C_2–C_4 alkanes (and/or alkenes) and condensable C_6–C_{12} aromatics such as benzene, toluene, xylene and naphthalene derivatives were analyzed by an on-line FID gas chromatograph using a six-way sampling valve heated at 533 K on a Porapak-P column and an one-line TCD GC for H_2, Ar, CO, CH_4 and CO_2 on an activated carbon column, similarly as reported elsewhere [10,13–15]. The condensable materials such as benzene, toluene, xylene, naphthalene, methylnaphthalene and anthracene were identified by using an off-line GC-MS (Perkin–Elmer, Auto System GC with 910 Q-Mass). Using an internal standard analyzing method with 10% Ar in the feed gas, methane conversion, selectivities of hydrocarbon products and coke formation formed on the catalysts were evaluated according to the mass balance for carbon.

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3. Results and discussion

The catalytic performances of 5%Re/HZSM-5 and Co-modified 5%Re/HZSM-5 for methane conversion without or with CO_2 at 873–1023 K and 1 and 3 atm pressure of methane are presented in table 1. It is clearly demonstrated that the Re-based HZSM-5 is a similarly active and selective catalyst in dehydrocondensation of methane as the Mo-based catalysts. Hydrogen is usually produced in large amounts (H_2/benzene $= 9$–12 mol/mol) by the dehydrocondensation of methane. At $\mathrm{SV} = 1440\ \mathrm{ml\,h^{-1}\,g\text{-}cat^{-1}}$, 973 and 1023 K, and 3 atm pressure the 5%Re/HZSM-5-based catalyst has stable activity for 6 h, as seen in table 1, Nos. 2–3 and 4–5. At 973 K, the total selectivity of gas-phase hydrocarbon products increases from 52% at the initial stage of the reaction to 64% and then keeps constant (72%) at the steady state of the reaction, while the selectivity of coke formation changes in a reverse way from 48 to 28%. Beyond 6 h of time-on-stream, the methane conversion gradually decreased from 6.4 to 2.8% on the Re/HZSM-5 with the time-on-stream of the reaction for 55 h, possibly due to the coke formation. As the methane conversion decreases, the naphthalene selectivity decreases at the expense of C_2 hydrocarbons, similarly on Mo/HZSM-5 catalysts [14,15]. It is of interest to find that the Re-based catalyst yields valuable products mainly consisting of C_2 hydrocarbons of ethene/ethane and benzene with minor by-products such as naphthalene and toluene, different from those on Mo/HZSM-5 [10,13–15]. Using 10% Ar in methane flow as the internal standard for the reaction analysis, the present work has been conducted to carefully evaluate the yields and selectivities of hydrocarbon products and coke formation in the conversion of methane. The coke consists not only of the amorphous and graphitic carbons, but also the deeply condensed aromatic compounds such as anthracene and tetracene in less than a few percent selectivity which are difficulty analyzed by the GC system due to the strong adsorption on the separation column [10,14,15].

A TG/DTA/mass study was performed using TG-DTA-2020S (Mac Science Co.) under a methane/He stream of 1 atm ($CH_4 = 15\ \mathrm{ml\,min^{-1}}$ and $\mathrm{He} = 150\ \mathrm{ml\,min^{-1}}$). 40–50 mg of the 5%Re/HZSM-5 catalyst was mounted in a fused alumina boat and the evolving products such as H_2, CO, H_2O, CO_2, C_2H_4, C_2H_6, C_6H_6 and $C_{10}H_8$ were continuously monitored with a Thermolab mass spectrometer (VG analysis) at $m/e = 2$, 18, 28, 44, 26, 30, 78 and 128, respectively. The reaction temperature was raised from room temperature to 973 K with a heating rate of 10 K/min and held there for 30 min. Before the reaction started, the catalyst was heated in a He stream at 873 K for 30 min and, in some cases, was further pretreated with H_2 and methane at 873 or 973 K, respectively. As shown in figure 1, the endothermal reaction and weight loss occurred in TG-DTA spectra at 830–895 K with a considerable evolution of CO ($m/e = 28$), CO_2 ($m/e = 44$) and H_2 ($m/e = 2$) with a trace of water ($m/e = 18$). This indicates that the starting rhenium oxide on the calcined Re/HZSM-5 is reduced with methane at 895 K. This initiates the methane conversion to C_2 products (ethene ($m/e = 26$) + ethane

Table 1
Catalytic performances of methane dehydrocondensation on 5%Re/HZSM-5-based catalyst.[a]

No.	Catalyst	Temp. (K)	Pressure (atm)	Conv.[b] (%)	Rate of formation[c] ($\mathrm{nmol\,s^{-1}\,g\text{-}cat^{-1}}$)			Selectivity[c] (%)			
					C_2 HC	Bz	Np	C_2 HC	Bz	Np	Coke
1	5%Re/HZSM-5	873	1	1.2	7	10	tr	15	60	–	23
2	5%Re/HZSM-5	973	3	7.0	19	61	26	3	29	21	44
3	5%Re/HZSM-5[d]	973	3	6.4	23	85	16	4	44	14	34
4	5%Re/HZSM-5	1023	3	9.3	29	117	16	4	42	10	42
5	5%Re/HZSM-5[d]	1023	3	8.1	36	128	5	5	53	3	35
6	3%Mo/HZSM-5 [14,15]	973	1	6.8	18	98	23	2	42	16	32
7	3%Mo/HZSM-5 [14,15]	1023	3	6.9	20	120	36	3	31	22	38
8	5%Re/HZSM-5	1023	3	9.3	161	497	0	6	52	0	38
9	5%Re/HZSM-5[d]	1023	3	1.6	231	37	0	46	22	0	27
10	5%Re/HZSM-5[e]	1023	3	9.7	101	471	173	4	57	35	0
11	5%Re/HZSM-5[d,e]	1023	3	8.5	129	581	76	5	73	16	0
12	3%Mo/HZSM-5[e]	1023	3	9.5	109	486	138	5	62	29	0
13	3%Mo/HZSM-5[d,e]	1023	3	7.3	134	465	60	7	72	16	0
14	5%Re–0.5%Co/HZSM-5[e]	1023	3	8.7	98	588	86	4	65	16	9
15	5%Re–0.5%Co/HZSM-5[d]	1023	3	2.6	240	138	0	29	51	6	6
16	5%Re–0.5%Co/HZSM-5[e]	1023	3	8.8	113	524	80	5	71	19	0
17	5%Re–0.5%Co/HZSM-5[d,e]	1023	3	5.4	205	303	16	16	70	6	0

[a] Inlet gas = 100% CH_4 except for [e], SV = 1440 $\mathrm{ml\,h^{-1}\,g\text{-}cat^{-1}}$ for entries Nos. 1–6 and 5000 $\mathrm{ml\,h^{-1}\,g\text{-}cat^{-1}}$ for entries Nos. 7–16, $C_2\ \mathrm{HC} = C_2H_4 + C_2H_6$, $\mathrm{Bz} = C_6H_6$ and $\mathrm{Np} = C_{10}H_8$.

[b] Methane conversion taken after 40–80 min time-on-stream except for [d].

[c] Product selectivity (%) on carbon basis among methane consumed.

[d] Data taken after 360 min time-on-stream.

[e] Inlet gas = 2% CO_2 + 98% CH_4, SV = 5000 $\mathrm{ml\,h^{-1}\,g\text{-}cat^{-1}}$.

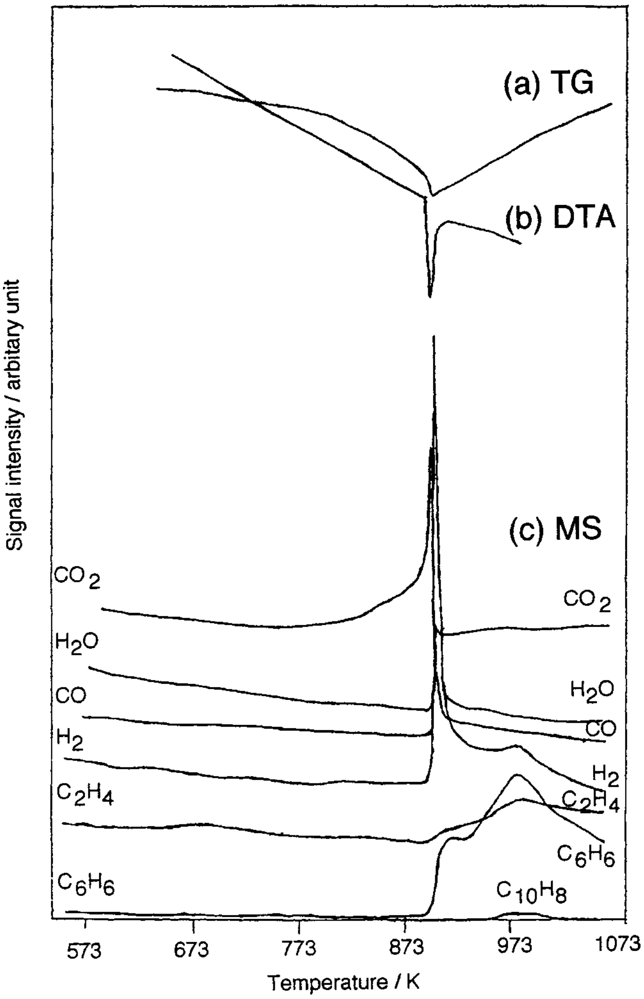


Figure 1. TG (a), DTA (b) and Mass (c) spectra of 5%Re/HZSM-5 (SiO_2/Al_2O_3 ratio of 40) in the methane reaction by programmed heating (10 K/min) from 300 to 973 K and holding at 973 K for 30 min. Gas flow rate: CH_4/He = 15/150 (ml/min) at 1 atm.

($m/e = 30$)), benzene ($m/e = 78$) and a trace of naphthalene ($m/e = 128$), accompanied with the hydrogen ($m/e = 2$) evolution at above 895 K. On the other hand, to characterize the active structure of the 5%Re/HZSM-5 in the methane aromatization reaction, Re L_{III}-edge EXAFS studies have been conducted using the 10B line at the Photon Factory of National Laboratory for the High Energy Physics (KEK-PF; Tsukuba, Japan). The Fourier transform spectra of the 5%Re/HZSM-5 sample after the reaction with methane at 573 and 973 K for 2 h represent the main Re–Re peak at 2.6 Å with a negligible contribution of Re–O and Re–C in the region of 1.5–2.0 Å. The structural information deduced from the curve fitting of the FT function for the samples after the reaction of Re/HZSM-5 with methane shows that the Re–Re distance (R) and coordination number (CN) are evaluated as $R = 2.74$–2.75 Å and CN = 4.0–6.4, respectively. The Re–Re distance in the metallic Re powder as the reference sample is 2.74 Å and CN = 12. The results suggest that the Re/HZSM-5 is reduced with methane at 875 K to the metallic particles of 10–20 Å which are highly dispersed on HZSM-5 zeolite. By contrast, the TG-DTA pattern in H_2/He flow (10/100 v/v) offers a broad band of weight loss and an exothermic peak at 473–673 K with the formation of water due to the successive reduction of rhenium oxide with hydrogen to Re metal [19]. It is of interest to find that the catalytic condensation of methane proceeded at 973 K on the Re/HZSM-5 reduced with hydrogen at 623 K for 1 h to provide C_2 hydrocarbons and benzene with a higher methane conversion and higher selectivities, compared with those on the fresh Re/HZSM-5. These data in TG/DTA/mass and EXAFS studies indicate that Re oxide on HZSM-5 is reduced with methane at temperature around 873 K to form reactive metallic Re in high dispersion on HZSM-5 which initiates the methane dehydrocondensation to C_2 hydrocarbons and benzene, which is different from the active Mo carbide formation in the reaction on Mo/HZSM-5 [14,15] at around 973 K.

The addition of CO to methane feed gas exerts a significant effect on the catalytic performances of Re/HZSM-5 for the dehydrocondensation of methane to form C_2 hydrocarbons and aromatics such as benzene and naphthalene at 873–1023 K, SV = 1440 $\mathrm{ml\,h^{-1}\,g\text{-}cat^{-1}}$ and 3 atm. The conversion and benzene formation rate were decreased gradually using pure methane in 20 h of reaction, while with the addition of CO in the feed gas, the methane conversion drop was substantially moderated and the formation rates of benzene keep the stationary level in the prolonged time-on-stream of 30 h. Increasing the partial pressure of CO (from 9 to 24%), as shown in figure 2, it is of interest to find that the rate of benzene formation was effectively enhanced by 1.5–2 times and also was stabilized at an almost constant level during the prolonged reaction. This suggests that the active carbon derived from CO by the Boudart reaction ($2CO \rightleftharpoons CO_2 + [C]$) is participating in forming benzene.

The catalyst performances on Re/HZSM-5 were also markedly improved by adding a few percent of CO_2 to the methane feed. The yields of hydrocarbons were enhanced and coke selectivities in the methane dehydrocondensation at 973–1023 K greatly reduced by addition of 1–3% CO_2 to methane, as shown in table 1. Methane conversion was stable at SV = 1440 $\mathrm{ml\,h^{-1}\,g\text{-}cat^{-1}}$ and 1023 K, while it dropped sharply at a more severe condition of SV = 5000 $\mathrm{ml\,h^{-1}\,g\text{-}cat^{-1}}$ (Nos. 7–8 and 13–14). However, the addition of 2% CO_2 in the methane feed dramatically improved the catalytic performances as seen for Nos. 9–10 and 15–16. Since a large amount of CO and a little amount of CO_2 were detected in the tail gas, it is suggested similarly on the Mo/HZSM-5 [14,15] that CO_2 is removing surface inactive carbon to produce double amount of CO under the reaction condition by the reverse Boudart process ($CO_2 + C \rightleftharpoons 2CO$). While, by contrast to the CO, an exceeding addition of CO_2 (>4–10%) to the methane feed substantially inhibited the formation of hydrocarbon products such as benzene. An excess addition of CO_2 to the methane feed results in the oxidation of Re sites on HZSM-5 which is inactive for the methane dehydrocondensation to benzene.

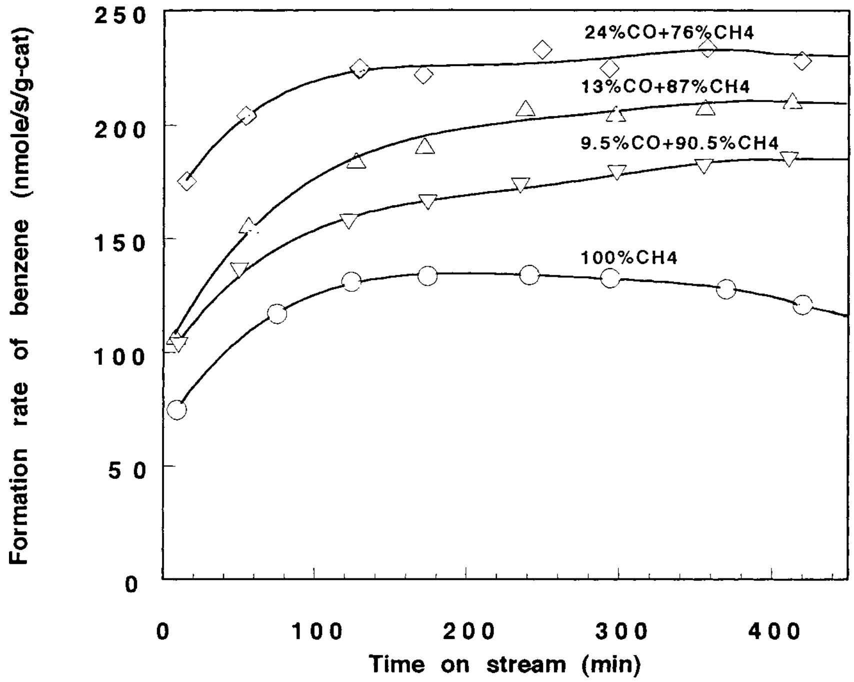
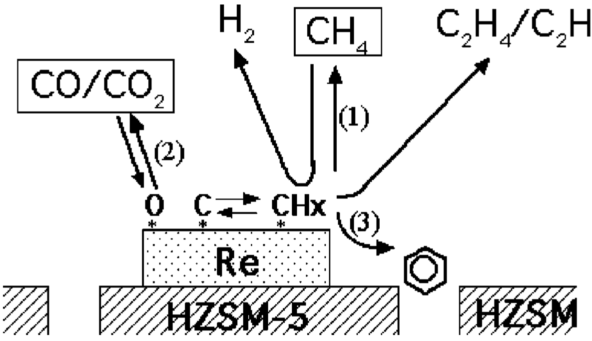


Figure 2. Catalytic performances of 5%Re/HZSM-5 for the rates of benzene formation in the dehydrocondensation of methane with or without the addition of CO to methane feed at 1023 K, 3 atm and SV = 1440 ml h^{-1} g-cat^{-1}.

The coke deposited on the catalyst surface after reaction was evaluated by a temperature-programmed oxidation (TPO) technique flowing a mixture gas of O_2 (20 ml/min) and He (150 ml/min) as the oxidant and the amount of CO_2 in the tail gas was analyzed by an on-line mass spectrometer. It was demonstrated by the TPO experiments that the amount of coke formed on the catalyst surface was greatly reduced by adding various amounts of CO (9–25%) or CO_2 (1–8%) to the methane feed gas. The increase of CO concentration from 9 to 25% resulted in a suppression of coke formation on the catalyst surface. The addition of CO_2 in the methane feed gas decreased effectively the coke deposition to a much lower level, which may be related to its higher oxidizing property, compared with that by CO addition. Accordingly, it was suggested that CO/CO_2 addition to methane not only effectively suppresses the coke formation but also yields active carbon [C]. Thus, the addition enhances substantially the rate of benzene formation and its stability.

Based on the above results and analogous discussion on the Mo/HZSM-5 catalysts [3–17], we suggest the mechanism of the catalytic dehydrocondensation of methane with CO/CO_2 on the new family of Re/HZSM-5-based catalysts towards ethylene, benzene, and naphthalene formation as depicted in scheme 1. Firstly, CH_4 and CO may dissociate on the metallic Re sites to form the active species such as [C] and [CH_x] through reactions (1) and (2). Then, the active carbon species [C] from methane and CO are hydrogenated to [CH_x] (possibly $x = 2$ carbene fragments), as illustrated in reaction (3), followed with the conversion of C_2 intermediates such as ethylene to higher hydrocarbons such as benzene and naphthalene in reaction (1) on the Re/HZSM-5 catalysts. On this regard, it is worthy to note that Re as well as Mo and W is one of the catalytic active elements for olefin metathesis via the carbene intermediates. In contrast to the molybdenum carbide (Mo_2C) as the active species for the reaction on the Mo/HZSM-5, EXAFS and TG/DTA/mass studies suggest that the metallic Re on HZSM-5 is responsible for the catalytic dehydrocondensation of methane towards C_2 hydrocarbons, benzene, and naphthalene.



Scheme 1.

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